

Mapping Capabilities of the FTIR Laboratory and Support of the Combinatorial Growth Efforts

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ABSTRACT

The combinatorial synthesis of thin films involves the deposition of material under various growth parameters onto a single substrate. This variation can be continuous (e.g. intentional composition gradients) or discrete (e.g. changes in the substrate temperature between subsequent growth runs). In either case, the benefits are the same - increased utilization of substrate material and growth time over that required to deposit a similar range of materials one at a time. This benefit becomes substantial when applied to the large parameter space associated with the research and development of new or novel materials.

Paramount to the success of this approach is the ability to efficiently characterize these heterogeneous films. In response to this need, the Fourier-Transform InfraRed (FTIR) Spectroscopy Laboratory has implemented several new mapping capabilities that allow for the quick and accurate measurement of Reflectance, Transmittance and Photoluminescence data over lateral dimensions ranging from tens of microns to several inches. The details of these capabilities will be presented in the context of current projects involving transparent conducting oxides, a-Si:H, and polycrystalline CuInGaSe₂ thin-films.

1. Fourier-Transform Characterization: Techniques

The infrared region of the electromagnetic spectrum spans from about 50 to 12,000 cm⁻¹ (0.006 to 1.5 eV) and is commensurate with the energy required to excite rotations or vibrations of the chemical bonds between the constituents of a compound. Consequently, this energy range is ideal for characterizing the chemical make-up of materials.

One common way to probe these transitions is to direct infrared radiation (I_0) onto the material of interest and measure the relative amount of this radiation that is either transmitted (I_T) or reflected (I_R). NREL utilizes an FTIR spectrometer to perform this function because of its improved signal-to-noise, resolution, accuracy, and reduced measurement time relative to dispersive spectrometers.

The resulting analysis of the FTIR spectrum involves two main steps: first, identifying the chemical bond associated with a specific observed transition energy; and second, quantifying the number of those bonds based on an analysis of the peak height or area. This approach is commonly used to characterize organic compounds, elemental impurities, and oxide precipitates in semiconductors. Examples of these include the identification of surface impurities that are a result of various deposition or processing steps, the quantification of

carbon and oxygen in crystalline silicon, and the measurement of hydrogen in amorphous silicon.

While the majority of FTIR work is focused on analyzing the chemical bond information, the technique is general in nature and can be used to analyze other infrared induced transitions. One example of this is the excitation and analysis of free charge carriers within a metal or semiconductor. In this case, the frequency dependence of the absorption process is a function of several important transport parameters including the density of carriers and their effective mass.

The advantages of the FT-technique are also utilized in Fourier-Transform Raman Spectroscopy and Fourier-Transform Photoluminescence Spectroscopy. Both techniques involve exciting the sample with a laser and spectrally resolving the emitted radiation. Raman Spectroscopy looks at the small portion of emitted radiation consisting of the laser-line shifted in energy by amounts equal to the vibrational modes of the material. Analysis of this shifted spectrum reveals information on the chemical bonds similar to that discussed above for the FTIR technique. Photoluminescence Spectroscopy analyzes the radiation emitted from electronic transitions and provides information on the bandgap and electron defect levels.

2. Fourier-Transform Characterization: Mapping

The abilities of the Fourier Transform technique described above provide vital information on the growth and understanding of PV-related materials. In response to the needs of the combinatorial growth efforts, these capabilities have been extended through the ability to perform measurements at individual points across the sample. This mapping capability is typically achieved by moving the sample, step-by-step, across the fixed probe-beam. The resulting increase in measurement time is a function of the number of measurement spots (lateral resolution), the time required to obtain a clean spectra, and the time required to move from one location to the next. Relying only on manual operation results in a time-consuming effort and reduces the overall value of the combinatorial approach. Because of this, the FTIR Spectroscopy Laboratory has implemented automated mapping capabilities on the mid-IR and FT-Raman/Photoluminescence systems.

One particularly good example of the power of these added capabilities is the mapping of large (2x2 inch and 4x4 inch) non-uniform transparent conducting oxide (TCO) films. In these films, composition gradients are intentionally introduced by the specific substrate-to-source configuration. Figure 1 is a map of the reflectance (at 2000 cm⁻¹) for a non-uniform 4x4 inch Cd₂SnO₄ film. As

mentioned above, the reflectivity can be related to the carrier concentration and the effective mass – two parameters influencing the film conductivity. Correspondingly, this data provides information on the uniformity of the conductivity. By correlating this with other measurements (e.g. composition) it becomes possible to more efficiently probe the large expanse of parameter space and ultimately find the conditions and composition required for the growth of suitable material.

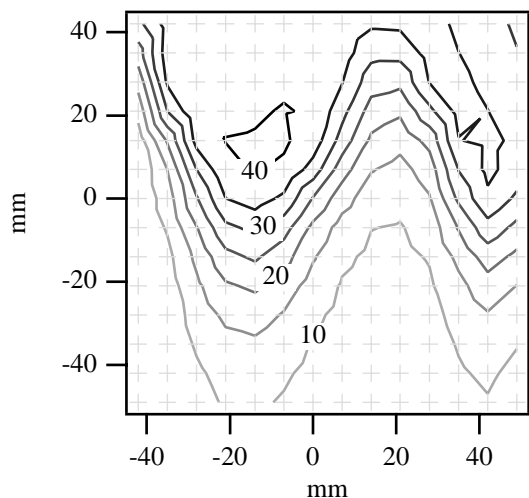


Fig 1. Contour map of the reflectance (at 2000 cm^{-1}) for a 4x4 inch Cd_2SnO_4 film deposited on glass.

Another example of the mapping capability involves the detection of H in a-Si:H. Figure 2 shows the result of analyzing transmittance data on a discrete 4x4 matrix of unique a-Si:H films grown on a crystalline silicon substrate. This FTIR data can be correlated with other information such as growth conditions, crystalline fraction, light and dark conductivity, etc. to more efficiently arrive at an understanding between the growth conditions, material composition, and material parameters.

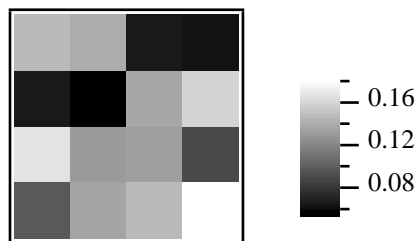


Fig 2. Hydrogen content of a discrete 4x4 matrix of a-Si:H films grown on a crystalline silicon substrate.

One final example of the automated mapping capability is the FT-PL data in Figure 3. In this case, the luminescence data provides a measure of the bandgap as a function of position. This type of linear map is often sufficient to characterize a film or growth system that is known to contain a non-uniformity along only one of the two lateral dimensions. This particular technique can be extended to area maps and the small spot size ($1\text{--}2\text{ }\mu\text{m}$)

allows for relatively high resolution maps of film properties such as the bandgap or luminescent impurity centers.

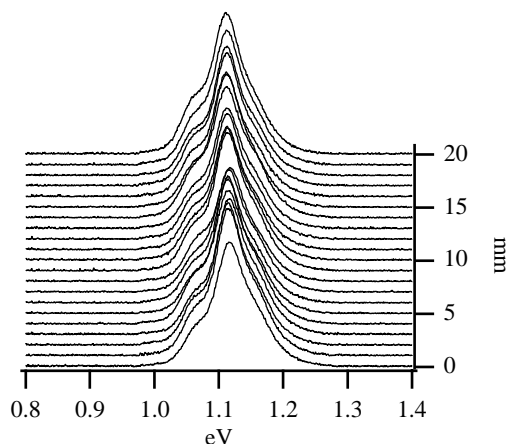


Fig 3. Fourier-Transform Photoluminescence data across a 1-inch section of a polycrystalline CuInGaSe_2 thin-film.

3. Fourier-Transform Characterization: Specifications

The general specifications for the FT-systems are summarized here. These are subject to change and adapt based on the needs of the PV Program.

Nicolet 510 & Magna 550 FT-IR Spectrometers:

Detector: Range	DTGS: 400 - 7,400 cm^{-1}
Detector: Range	MCT/B: 400 - 6,400 cm^{-1}
Spot Size	$\leq 13\text{ mm}$
Map Size	$\leq 8\text{ inch diameter}$

Nicolet Continuum & Nic-Plan IR Microscopes:

Detector: Range	MCT/A: 650 - 6,400 cm^{-1}
Detector: Range	MCT/A*: 750 - 6,400 cm^{-1}
Spot Size	10 - 150 μm or 50 - 300 μm
Map Size	$\leq 2\text{x}3$ or $1\text{x}4$ inches

Nicolet 20F Far IR Spectrometer:

Detector: Range	DTGS: 50 - 600 cm^{-1}
Spot Size	$\leq 13\text{ mm}$
Map Area	currently not available

Nicolet FT-Raman 960 & MicroRaman Accessory:

Detector: Range	InSb: 3,700 - 10,000 cm^{-1}
Detector: Range	Ge: 5,400 - 12,400 cm^{-1}
Spot Size	1 - 2 μm , 10 μm , or 100 μm
Map Area	$\leq 1\text{x}3\text{ in. w/small spot sizes}$

4. Summary

The FTIR Spectroscopy Laboratory has enhanced its support of the PV Program through the incorporation of automated mapping capabilities. The result of this is the ability to probe the non-uniformities, either intentional or not, that are found in the various materials and growth systems.

5. Acknowledgements

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